Supplementary Information

Copper-Mediated Annulation of 2-(1-Arylvinyl)anilines and Aryl Nitrosos towards 2,3-Diaryl-2H-Indazoles

Weiming Hu, Jin-Tao Yu, Suqin Liu, Yan Jiang and Jiang Cheng*

School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, Jiangsu Province Key Laboratory of Fine Petrochemical Engineering, Changzhou University, Changzhou 213164, P. R. China

Email: jiangcheng@cczu.edu.cn

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1. General Considerations

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. \(^1\)H NMR，\(^{13}\)C NMR and \(^{19}\)F spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for \(^{13}\)C and 282 MHz for \(^{19}\)F). NMR experiments are reported in \(\delta\) units, parts per million (ppm), and were referenced to CDCl₃ (\(\delta 7.26\) or 77.0 ppm) as the internal standard. The coupling constants \(J\) are given in Hz. High-resolution mass spectra (HRMS) were obtained using a Bruker micro-TOF II focus spectrometer (ESI). IR spectra were recorded on a spectrometer using KBr discs. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). All melting points were uncorrected.

2. Synthesis and Reaction

Synthesis of 2-(1-substituted vinyl) anilines were synthesized according to the literature methods.

Substrates 1a-1f, 1h, 1j-1m were synthesized according to Method A:¹

Method A:

\[
\begin{align*}
\text{Ar} & \quad + \quad \text{NH}_2 \\
\text{Ar} & \quad \xrightarrow{\text{KSF, xylene}} \quad \text{Ar} \quad \text{Ar}
\end{align*}
\]

Under air, anilines (9.0 mmol), phenylacetylenes (18.0 mmol) and 1.7 g of montmorillonite KSF were added to 150 mL of xylene in a round-bottomed flask. The flask was stirred and heated in an oil bath to 140 °C, under a reflux condenser (running cold water as the coolant) that was connected at its top to a paraffin bubbler. After 18 h, the reaction mixture was cooled to room temperature and purified directly by flash chromatography with a gradient of hexane to hexane/ethyl acetate \((V_1/V_2 = 60/1)\), followed by distillation under vacuum to afford corresponding 2-(1-arylvinyl) anilines.

Substrates 1g, 1i, 1n and 1o-1r were synthesized according to Method B:²

Method B:
Under N₂, a well stirred mixture of tosylhydrazone (7.5 mmol), 2-iodoaniline (5 mmol), Pd(PPh₃)₂Cl₂ (2.5 mol%) in 1,4-dioxane (56 mL) was heated at 100°C. To this hot clear solution was added t-BuOLi (1.6 g, 20 mmol), and the reaction was stirred at 100°C for 3 h. Then, the reaction mixture was cooled to room temperature and diluted with EtOAc (60 mL) and passed through a short Celite pad; the solvent was evaporated under reduced pressure, and purified on a silica gel column (hexane/EtOAc, 90:1) to obtain corresponding products.

**Synthesis of nitrosobenzenes³**

Under N₂, aniline (20 mmol) was dissolved in DCM (50 mL). Then the solution of oxone (22 mmol, 13.5 g) in 50 mL of water was added slowly. The reaction mixture was stirred at room temperature till full consumption of the starting material as monitored by TLC (about 30 min.). After that, the reaction mixture was separated and extracted with DCM (15 mL × 3). The combined organic layers were washed with HCl (1 M) then saturated Na₂CO₃ and brine. After dried by anhydrous Na₂SO₄, the solvent was evaporated, and the crude mixture was purified by flash column chromatography on silica gel with hexane to afford analytically pure aryl nitroso.

**Synthesis of (E)-phenyl(2-(phenyldiazenyl)phenyl)methanone (5)⁴**

A mixture of azobenzene (0.3 mmol), benzooylformic acid (0.33 mmol), Pd(OAc)₂ (6.8 mg, 0.03 mmol), K₂S₂O₈ (162.3 mg, 0.6 mmol) in 1,4-dioxane/AcOH/DMSO (7/2/1, V/V/V, 2 mL) was stirred at 80°C for 10 h. The mixture was filtered by a silica gel plug with ethyl acetate as the eluent and evaporated in vacuum. The product was
purified by column chromatography over silica gel using petroleum ether and ethyl acetate (20:1) as the eluent. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 7.8$ Hz, 1H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.69-7.58 (m, 3H), 7.51-7.43 (m, 3H), 7.40-7.32 (m, 5H).

**Synthesis of 1-(2-aminophenyl)-1-phenylethane-1,2-diol (6)**

![Chemical structure](image_url)

**General procedure for $N$-protection**

To a magnetically stirred mixture of 2-(1-phenylvinyl)aniline (1 mmol) and (Boc)$_2$O (1 mmol), a catalytic amount of iodine (10 mol %) was added under solvent-free conditions at room temperature. After stirring for 12 h, diethyl ether (10 mL) was added. The reaction mixture was washed with Na$_2$S$_2$O$_3$ (5%, 5 mL) and saturated NaHCO$_3$ and dried over Na$_2$SO$_4$, the solvent was rotavaped under reduced pressure, and the residue was purified by silica gel column chromatography (hexane/EtOAc, $V_1/V_2 = 60:1$) to afford the product $t$-butyl (2-(1-phenylvinyl)phenyl)carbamate in 89% yield as a yellowish oil.

**General procedure for dihydroxylation**

$t$-Butyl (2-(1-phenylvinyl)phenyl)carbamate (59 mg, 0.2 mmol), NMO (28 mg, 0.24 mmol), [bmim]PF$_6$ (0.1 mL), OsO$_4$ (1 mg, 2 mol %), DMAP (0.6 mg, 2.4 mol%), H$_2$O (0.1 mL), $t$-BuOH (0.2 mL) were added to a flask. Then the reaction mixture was stirred at rt for 16 h under air atmosphere. The ionic liquid layer was extracted with ethyl acetate (6 mL × 3). The combined extracts were concentrated and purified by flash silica gel column chromatography (hexane/EtOAc, $v_1/v_2 = 3:1$) to afford the product $t$-butyl (2-(1,2-dihydroxy-1-phenylethyl)phenyl)carbamate in 85% yield as a reddish oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.08 (s, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.35-7.28 (m, 6H), 7.25-7.23 (m, 1H), 7.10-7.05 (m, 1H), 4.33 (d, $J = 11$ Hz, 1H), 3.88 (d, $J = 11$ Hz, 1H), 2.07 (s, 1H), 1.60 (s, 1H), 1.29 (s, 9H).

**General procedure for $N$-deprotection**

Under air, a 20 mL of Schlenk tube equipped with a stir bar was charged with
tert-butyl (2-(1,2-dihydroxy-1-phenylethyl)phenyl)carbamate (0.2 mmol) was added 4.0 mL of water. Then the reaction mixture was stirred for 6 h at 100 °C (monitored by TLC). After that, the reaction mixture was cooled down and extracted with ethyl acetate (6 mL×3). The extract was washed with brine, dried over anhydrous Na₂SO₄, and then concentrated in vacuum. The residue was purified by column chromatography (hexane/EtOAc, V₁/V₂ = 3:1) to afford the product 1-(2-aminophenyl)-1-phenylethane-1,2-diol in 75% yield as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.27 (m, 6H), 7.17-7.12 (m, 1H), 6.89-6.84 (m, 1H), 6.67-6.64 (m, 1H), 4.25 (d, J = 11 Hz, 1H), 3.84 (d, J = 11 Hz, 1H), 3.34 (br, 3H), 1.26 (s, 1H).

Annulation of 2-(1-Substituted vinyl) Anilines and Aryl Nitrosos

\[
\begin{align*}
\text{NH}_2 & \quad \text{Ar}^1 & \quad \text{Ar}^2 & \quad \text{Ar}^3& \quad \text{NO} \\
\text{Cu(OAc)}_2 (2 \text{ equiv}, \text{O}_2) & \quad \text{DMSO, 130 °C, 15 h} \\
\end{align*}
\]

Scheme 1. Annulation of 2-(1-Substituted vinyl) Anilines and Aryl Nitrosos

Under O₂, a 20 mL of Schlenk tube equipped with a stir bar was charged with 2-(1-arylvinyl) anilines (0.1 mmol), aryl nitrosos (0.25 mmol), Cu(OAc)₂ (0.2 mmol), DMSO (2.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 130 °C for 15 h in oil bath. After the completion of the reaction, 6 mL of saturated brines was added to the mixture, and extracted with ethyl acetate (8 mL × 3) with ethyl acetate. The combined organic extracts were dried over anhydrous Na₂SO₄. Subsequently, the solvent was filtered and evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V₁/V₂, 30:1) as the eluent to give the desired products.
3. Research of Mechanism

![Chemical Structures]

**Scheme S1. Mechanism Studies**

**General procedure for the reaction of 4 and 2 (Scheme S1, Eq 1)**

Under O₂, a 20 mL of Schlenk tube equipped with a stir bar was charged with 4 (0.1 mmol), aryl nitrosos 2 (0.25 mmol), Cu(OAc)₂ (0.2 mmol), DMSO (2.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 130 °C for 15 h in oil bath.

**General procedure for the reaction of 5 (Scheme S1, Eq 2)**

Under O₂, a 20 mL of Schlenk tube equipped with a stir bar was charged with 5 (0.1 mmol), Cu(OAc)₂ (0.2 mmol), DMSO (2.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 130 °C for 15 h in oil bath.

**General procedure for the reaction of 6 and 2 (Scheme S1, Eq 3)**

Under O₂, a 20 mL of Schlenk tube equipped with a stir bar was charged with 6 (0.1 mmol), aryl nitrosos 2 (0.25 mmol), Cu(OAc)₂ (0.2 mmol), DMSO (2.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 130 °C for 15 h in oil bath. Product 3aa was formed in 28 yield, byproduct O-3aa was formed in 37 yield. ¹H NMR for O-3aa (300 MHz, CDCl₃) δ 8.19 (d, J = 8 Hz, 1H), 7.85-7.80 (m, 4H), 7.67-7.58 (m, 2H), 7.51-7.38 (m, 5H), 7.36-7.30 (m, 2H); ¹³C NMR for O-3aa (300 MHz, CDCl₃) δ 142.1, 137.7, 137.3, 135.5, 135.3, 132.8, 131.9, 131.0, 129.8, 129.0, 128.60, 128.56, 128.3, 123.4, 122.2.
Under N₂, a 20 mL of Schlenk tube equipped with a stir bar was charged with 6 (0.1 mmol), aryl nitrosos 2 (0.25 mmol), Cu(OAc)₂ (0.2 mmol), DMSO (2.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 130 °C for 15 h in oil bath.

Under O₂, a 20 mL of Schlenk tube equipped with a stir bar was charged with 6 (0.1 mmol), aryl nitrosos 2 (0.25 mmol), DMSO (2.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 130 °C for 15 h in oil bath.

Under N₂, a 20 mL of Schlenk tube equipped with a stir bar was charged with 6 (0.1 mmol), aryl nitrosos 2 (0.25 mmol), DMSO (2.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 130 °C for 15 h in oil bath.

4. GC-MS Data of Compounds 3ca, 3ea, 3ka and 3 ma

![GC-MS data of 3ca and O-3ca](image)

**O-3ca, [M-1]^+ = 319**

![GC-MS data of 3ea and O-3ea](image)

**O-3ea, [M]^+ = 304**
**5. Characterization Data for the Products**

_2,3-diphenyl-2H-indazole (3aa):_\(^8\)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3aa (20.3 mg, 75% yield) as a yellowish oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.82 (d, \(J = 8.8\) Hz, 1H), 7.73 (d, \(J = 8.5\) Hz, 1H), 7.47-7.43 (m, 2H), 7.41-7.36 (m, 9H), 7.17-7.13 (m, 1H), \(\delta\) 148.9, 140.2, 135.4, 129.9, 129.6, 128.9, 128.7, 128.3, 128.2, 127.0, 126.0, 122.5, 121.7, 120.5, 117.7; IR (KBr) 3058, 1735, 1626, 1597, 1504, 1455, 1363 cm\(^{-1}\).
5-\((\text{tert-butyl})-2,3\)-diphenyl-2\(H\)-indazole (3ba):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3\(\text{ba}\) (20.5 mg, 63\% yield) as a yellowish oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.77 (d, \(J\) = 9.1 Hz, 1H), 7.60 (s, 1H), 7.51 (d, \(J\) = 9.2 Hz, 1H), 7.42-7.36 (m, 10H), 1.39 (s, 9H); \(^1^3\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 147.9, 145.4, 140.4, 135.3, 130.3, 129.8, 129.0, 128.9, 128.23, 128.15, 126.9, 126.1, 121.6, 117.4, 114.4, 35.0, 31.3; HRMS (ESI) m/z calcd for C\(_{23}\)H\(_{23}\)N\(_2\) (M+H)\(^+\) 327.1856, found 327.1860; IR (KBr) 3061, 2960, 2926, 1596, 1538, 1502, 1457, 1365, 1311 cm\(^{-1}\).

5-chloro-2,3-diphenyl-2\(H\)-indazole (3ca):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3\(\text{ca}\) (21.6 mg, 71\% yield) as a yellowish oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.74 (d, \(J\) = 9.2 Hz, 1H), 7.69 (s, 1H), 7.44-7.38 (m, 8H), 7.34-7.28 (m, 3H); \(^1^3\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 147.3, 139.9, 135.2, 129.5, 129.3, 129.0, 128.9, 128.6, 128.5, 128.4, 128.1, 125.9, 122.1, 119.3, 119.2; HRMS (ESI) m/z calcd for C\(_{19}\)H\(_{14}\)ClN\(_2\) (M+H)\(^+\) 305.0840, found 305.0844; IR (KBr) 3063, 1597, 1499, 1454, 1340, 1321 cm\(^{-1}\).

5-methoxy-2,3-diphenyl-2\(H\)-indazole (3da):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3\(\text{da}\) (19.5 mg, 65\% yield) as a yellowish solid. m.p. 145-146 \(^\circ\)C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.73 (d, \(J\) = 9.3 Hz, 1H), 7.43-7.37 (m, 10H), 7.11 (d, \(J\) = 9.2 Hz, 1H), 6.93 (s, 1H), 3.86 (s, 3H); \(^1^3\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 155.9, 145.9, 140.3, 134.2, 130.3, 129.5, 128.9, 128.8, 128.0, 127.97, 125.8, 122.1, 121.6, 119.2, 96.2, 55.4; IR (KBr) 3060, 2998, 1634, 1596, 1505, 1457, 1325 cm\(^{-1}\).

5-fluoro-2,3-diphenyl-2\(H\)-indazole (3ea):
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3ea (19.3 mg, 67% yield) as a white solid. m.p. 113-114 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.80-7.76 (m, 1H), 7.43-7.38 (m, 8H), 7.33-7.28 (m, 3H), 7.19- 7.15 (m, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 159.0 (d, $J_{C,F} = 240$ Hz), 146.4, 140.1, 135.6 (d, $J_{C,F} = 8.0$ Hz), 129.6, 129.4, 129.0, 128.8, 128.41, 128.38, 125.9, 121.0 (d, $J_{C,F} = 12$ Hz), 119.9 (d, $J_{C,F} = 10$ Hz), 118.6 (d, $J_{C,F} = 29$ Hz), 102.9 (d, $J_{C,F} = 24$ Hz); $^{19}$F NMR (CDCl$_3$, 282 MHz) $\delta$ -119.13; HRMS (ESI) m/z calcd for C$_{19}$H$_{14}$FN$_2$ (M+H)$^+$ 289.1136, found 289.1140; IR (KBr) 3064, 1635, 1597, 1528, 1505, 1456, 1344, 1326 cm$^{-1}$.

5-bromo-2,3-diphenyl-2H-indazole (3fa):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3fa (20.2 mg, 58% yield) as a yellowish oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.87 (s, 1H), 7.69 (d, $J = 9.1$ Hz, 1H), 7.44-7.38 (m, 9H), 7.34-7.31 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 147.3, 139.9, 135.0, 130.6, 129.5, 129.3, 129.0, 128.9, 128.6, 128.5, 125.9, 122.9, 122.7, 119.5, 115.9; HRMS (ESI) m/z calcd for C$_{19}$H$_{14}$BrN$_2$ (M+H)$^+$ 349.0335, found 349.0338; IR (KBr) 3061, 2958, 1597, 1535, 1504, 1455, 1341, 1320 cm$^{-1}$.

5-methyl-2,3-diphenyl-2H-indazole (3ga):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3ga (19.9 mg, 70% yield) as yellowish oil. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.44 (d, $J = 8.8$ Hz, 1H), 7.48-7.37 (m, 11H), 7.23 (d, $J = 8.9$ Hz, 1H), 2.46 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 148.0, 140.3, 134.4, 131.9, 130.1, 129.9, 129.6, 128.9, 128.7, 128.10, 128.07, 125.9, 122.0, 118.4, 117.4, 21.8; HRMS (ESI) m/z calcd for C$_{20}$H$_{17}$N$_2$ (M+H)$^+$ 285.1386, found 285.1390; IR (KBr) 3057, 2958, 1597, 1535, 1504, 1455, 1398, 1345 cm$^{-1}$.

2,3,5-triphenyl-2H-indazole (3ha):
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give \(3\text{ha}\) (24.9, 72% yield) as a reddish solid. m.p. 134 - 135 °C; \(^1\text{H NMR}\) (CDCl\(_3\), 300 MHz) \(\delta 7.92-7.89\) (m, 2H), \(7.70-7.65\) (m, 3H), \(7.49-7.35\) (m, 13H); \(^{13}\text{C NMR}\) (CDCl\(_3\), 100 MHz) \(\delta 148.5, 141.6, 140.1, 135.9, 135.8, 129.8, 129.7, 129.0, 128.8, 128.7, 128.4, 128.3, 127.7, 127.2, 126.9, 125.9, 122.2, 118.2, 118.1; HRMS (ESI) m/z calcd for C\(_{25}\)H\(_{19}\)N\(_2\) (M+H)\(^+\) 347.1543, found 347.1544; IR (KBr) 3057, 1597, 1497, 1485, 1343, 1307 cm\(^{-1}\).

2-phenyl-3-(o-tolyl)-2\(H\)-indazole (3ia):\(^{8a,10}\)

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give \(3\text{ia}\) (15.1 mg, 53% yield) as a reddish oil. \(^1\text{H NMR}\) (CDCl\(_3\), 400 MHz) \(\delta 7.85\) (d, \(J = 8.8\) Hz, 1H), \(7.48-7.27\) (m, 11H), \(7.14-7.10\) (m, 1H), 1.98 (s, 3H); \(^{13}\text{C NMR}\) (CDCl\(_3\), 100 MHz) \(\delta 148.8, 140.4, 137.8, 135.2, 131.1, 130.6, 129.6, 129.2, 128.9, 127.9, 127.0, 126.0, 124.8, 122.6, 122.1, 120.7, 117.7, 19.9; IR (KBr) 3057, 2963, 1626, 1597, 1502, 1455, 1361, 1313 cm\(^{-1}\).

4,6-dimethyl-2,3-diphenyl-2\(H\)-indazole (3ja):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give the product \(3\text{ja}\) (11.3 mg, 38% yield) as a reddish oil. \(^1\text{H NMR}\) (CDCl\(_3\), 300 MHz) \(\delta 7.32-7.18\) (m, 11H), 6.61 (s, 1H), 2.36 (s, 3H), 2.06 (s, 3H); \(^{13}\text{C NMR}\) (CDCl\(_3\), 100 MHz) \(\delta 149.5, 140.2, 136.8, 136.0, 131.4, 131.3, 131.0, 128.63, 128.61, 128.0, 127.8, 125.9, 125.4, 120.2, 113.7, 22.1, 19.9; IR (KBr) 3058, 2958, 1625, 1596, 1504, 1443, 1363 cm\(^{-1}\).
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3ka (25.4 mg, 80% yield) as a reddish oil. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.68 (d, $J = 8.9$ Hz, 1H), 7.38-7.31 (m, 8H), 7.26-7.17 (m, 3H), 2.40 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 147.9, 140.0, 134.2, 133.1, 132.3, 130.8, 130.0, 129.1, 129.0, 128.5, 125.9, 121.9, 118.0, 117.5, 21.8; HRMS (ESI) m/z calcd for C$_{20}$H$_{16}$ClN$_2$ (M+H)$^+$ 319.0997, found 319.0998; IR (KBr) 3047, 2919, 1597, 1503, 1455, 1345, 1322 cm$^{-1}$.

5-methyl-2-phenyl-3-(p-tolyl)-2H-indazole (3la):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3la (23.2 mg, 78% yield) as a reddish solid. m.p. 125-126 °C; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.69 (d, $J = 8.9$ Hz, 1H), 7.44-7.34 (m, 6H), 7.24-7.17 (m, 5H), 2.42 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 1147.9, 140.3, 138.1, 134.5, 131.7, 129.8, 129.5, 129.4, 128.9, 128.0, 127.1, 125.9, 121.9, 118.5, 117.3, 21.8, 21.3; HRMS (ESI) m/z calcd for C$_{21}$H$_{19}$N$_2$ (M+H)$^+$ 299.1543, found 299.1549; IR (KBr) 3056, 3019, 2960, 1597, 1539, 1509, 1497, 1455, 1345, 1324 cm$^{-1}$.

5-chloro-3-(4-chlorophenyl)-2-phenyl-2H-indazole (3ma):$^{11}$

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3ma (20.6 mg, 61% yield) as a yellowish oil. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.74 (d, $J = 9.2$ Hz, 1H), 7.64 (d, $J = 1.2$ Hz, 1H), 7.41-7.36 (m, 7H), 7.32-7.23 (m, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 149.0, 139.9, 134.1, 132.1, 131.1, 129.2, 128.8, 128.5, 127.1, 126.0, 122.9, 122.7, 121.6, 120.1, 117.9; IR (KBr) 3065, 1596, 1500, 1453, 1341, 1319 cm$^{-1}$.

3-(4-chlorophenyl)-2-phenyl-2H-indazole (3na):$^{8,10,11}$
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3na (19.2 mg, 63% yield) as a yellowish oil. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.79 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.40-7.33 (m, 8H), 7.29-7.24 (m, 2H), 7.17-7.12 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 148.9, 139.9, 134.4, 134.1, 130.8, 129.13, 129.10, 128.5, 128.3, 127.1, 126.0, 122.8, 121.7, 120.1, 117.9; IR (KBr) 3059, 1596, 1502, 1454, 1363, 1297 cm$^{-1}$.

3-(4-bromophenyl)-2-phenyl-2H-indazole (3oa):$^{8,10,11,12}$

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3oa (19.2 mg, 45% yield) as a yellowish oil. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.81 (d, $J = 8.8$ Hz, 1H), 7.68 (d, $J = 8.5$ Hz, 1H), 7.54-7.51 (m, 2H), 7.41-7.35 (m, 6H), 7.24-7.14 (m, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 149.0, 139.9, 134.1, 132.1, 131.1, 129.2, 128.8, 128.5, 127.1, 126.0, 122.9, 122.7, 121.6, 120.1, 117.9; IR (KBr) 3058, 1598, 1502, 1454, 1397, 1361 cm$^{-1}$.

2-phenyl-3-(m-tolyl)-2H-indazole (3pa):$^{8a,10a,12}$

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3pa (21.6 mg, 76% yield) as a yellowish solid. m.p. 101-102 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.82 (d, $J = 8.7$ Hz, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.46-7.36 (m, 6H), 7.29-7.23 (m, 2H), 7.19-7.11 (m, 3H), 2.35 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 148.9, 140.2, 138.4, 135.5, 130.2, 129.7, 129.1, 128.9, 128.6, 128.2, 126.9, 126.8, 125.9, 122.3, 121.7, 120.6, 117.7, 21.4; IR (KBr) 3057, 3022, 2966, 1593, 1551, 1455, 1355, 1329 cm$^{-1}$.

3-(3-methoxyphenyl)-2-phenyl-2H-indazole (3qa):$^{8a}$
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3qa (21.0 mg, 70% yield) as a yellowish solid. m.p. 148-149 °C; 1H NMR (CDCl3, 400 MHz) δ 7.81 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 8.5 Hz, 1H), 7.47-7.36 (m, 6H), 7.30 (t, J = 7.9 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.96-6.89 (m, 3H), 3.70 (s, 3H); 13C NMR (CDCl3, 100 MHz) δ 159.6, 148.9, 140.2, 135.2, 131.0, 129.8, 129.0, 128.3, 127.0, 126.0, 122.5, 122.1, 121.6, 120.5, 117.7, 114.9, 114.2, 55.2; IR (KBr) 3061, 2988, 1635, 1593, 1500, 1455, 1335 cm⁻¹.

3-(3-chlorophenyl)-2-phenyl-2H-indazole (3ra):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3ra (20.7 mg, 68% yield) as a reddish oil. 1H NMR (CDCl3, 400 MHz) δ 7.82 (d, J = 8.7 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.42-7.28 (m, 9H), 7.8 (t, J = 7.4 Hz, 2H); 13C NMR (CDCl3, 100 MHz) δ 148.9, 139.8, 134.7, 133.7, 131.6, 130.0, 129.4, 129.1, 128.6, 128.4, 127.8, 127.1, 126.0, 123.0, 121.7, 120.1, 117.9; IR (KBr) 3064, 1588, 1512, 1455, 1368, 1290 cm⁻¹.

3-phenyl-2-(p-tolyl)-2H-indazole (3ab):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3ab (12.8 mg, 45% yield) as a yellowish oil. 1H NMR (CDCl3, 300 MHz) δ 7.80 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.41-7.29 (m, 8H), 7.19-7.11 (m, 3H), 2.38 (s, 3H); 13C NMR (CDCl3, 100 MHz) δ 1148.8, 138.2, 137.7, 135.3, 130.0, 129.7, 129.6, 128.7, 128.2, 126.9, 125.7, 122.4, 121.7, 120.5, 117.7, 21.2; HRMS (ESI) m/z calcd for C20H17N2 (M+H)+ 285.1386, found 285.1390; IR (KBr) 3058, 2960, 1625, 1601, 1351, 1461, 1363 cm⁻¹.
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3ac (20.5 mg, 63% yield) as a yellowish oil. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.80 (d, $J = 8.8$ Hz, 1H), 7.72 (d, $J = 8.5$ Hz, 1H), 7.41-7.34 (m, 10H), 7.16-7.11 (m, 1H), 1.33 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 151.4, 148.8, 137.6, 135.2, 130.0, 129.7, 128.7, 128.2, 126.8, 125.9, 125.4, 122.4, 121.7, 120.5, 117.7, 34.7, 31.3; HRMS (ESI) m/z calcd for C$_{23}$H$_{23}$N$_2$ (M+H)$^+$ 327.1856, found 327.1856; IR (KBr) 3059, 2961, 1625, 1601, 1517, 1497, 1461, 1363 cm$^{-1}$.

2-(3,5-dimethylphenyl)-3-phenyl-2H-indazole (3ad):$^{9,10a,12}$

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3ad (17.6 mg, 59% yield) as a yellowish oil. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.80 (d, $J = 8.7$ Hz, 1H), 7.72 (d, $J = 8.5$ Hz, 1H), 7.40-7.34 (m, 6H), 7.16-7.11 (m, 1H), 7.04 (s, 2H), 7.00 (s, 1H), 2.27 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 148.8, 140.0, 138.7, 135.3, 130.0, 129.9, 129.6, 128.6, 128.2, 126.8, 123.7, 122.3, 121.6, 120.5, 117.7, 21.2; IR (KBr) 3057, 2963, 1611, 1596, 1497, 1445, 1363 cm$^{-1}$.

2-(4-chlorophenyl)-3-phenyl-2H-indazole (3ae):$^{13}$

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3ae (17.3 mg, 57% yield) as a yellowish solid. m.p. 118-119 °C; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.79 (d, $J = 8.8$ Hz, 1H), 7.70 (d, $J = 8.5$ Hz, 1H), 7.43-7.34 (m, 10H), 7.17-7.12 (m, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 149.1, 138.7, 135.5, 134.1, 129.7, 129.6, 129.2, 128.9, 128.6, 127.3, 127.1, 122.7, 121.8, 120.4, 117.7; IR (KBr) 3059, 1626, 1599, 1501, 1445, 1364, 1301 cm$^{-1}$.
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3af (18.8 mg, 62% yield) as a yellowish oil. $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.79 (d, $J = 8.8$ Hz, 1H), 7.70 (d, $J = 8.6$ Hz, 1H), 7.59-7.57 (m, 1H), 7.44-7.33 (m, 7H), 7.27-7.23 (m, 2H), 7.17-7.12 (m, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 149.1, 141.2, 134.7, 133.0, 131.9, 129.8, 129.6, 129.5, 128.9, 128.6, 128.4, 127.4, 126.2, 124.1, 127.8, 120.5, 117.7; HRMS (ESI) m/z calcld for C$_{19}$H$_{14}$ClN$_2$ (M+H)$^+$ 305.0840, found 305.0840; IR (KBr) 3059, 1664, 1626, 1592, 1499, 1482, 1362 cm$^{-1}$.

2-(3-bromophenyl)-3-phenyl-2H-indazole (3ag):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give 3ag (21.9 mg, 63% yield) as a yellowish oil. $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.77-7.75 (m, 2H), 7.70 (d, $J = 8.5$ Hz, 1H), 7.52-7.48 (m, 1H), 7.44-7.34 (m, 6H), 7.26-7.12 (m, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 149.1, 141.2, 135.6, 134.9, 133.0, 131.3, 130.0, 129.7, 129.0, 128.9, 128.6, 127.4, 124.5, 122.8, 122.5, 120.5, 117.7; HRMS (ESI) m/z calcld for C$_{19}$H$_{14}$BrN$_2$ (M+H)$^+$ 349.0335, found 349.0339; IR (KBr) 3059, 1664, 1588, 1499, 1480, 1362 cm$^{-1}$. 
6. Reference


7. Copies of the $^1$H NMR, $^{13}$C NMR Spectra

2,3-diphenyl-2H-indazole (3aa):
5-(*tert*-butyl)-2,3-diphenyl-2H-indazole (3ba):
5-chloro-2,3-diphenyl-2H-indazole (3ca):
5-methoxy-2,3-diphenyl-2H-indazole (3da):
5-fluoro-2,3-diphenyl-2H-indazole (3ea):
5-bromo-2,3-diphenyl-2H-indazole (3fa):
5-methyl-2,3-diphenyl-2H-indazole (3ga)
2,3,5-triphenyl-2H-indazole (3ha):
2-phenyl-3-(o-tolyl)-2H-indazole (3ia):
4,6-dimethyl-2,3-diphenyl-2H-indazole (3ja):
3-(4-chlorophenyl)-5-methyl-2-phenyl-2H-indazole (3ka):
5-methyl-2-phenyl-3-(p-tolyl)-2H-indazole (3la):
5-chloro-3-(4-chlorophenyl)-2-phenyl-2H-indazole (3ma):
3-(4-chlorophenyl)-2-phenyl-2H-indazole (3na):

![Chemical Structure Image]

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3-(4-bromophenyl)-2-phenyl-2H-indazole (3oa):
2-phenyl-3-(m-tolyl)-2H-indazole (3pa):
3-(3-methoxyphenyl)-2-phenyl-2H-indazole (3qa):
3-(3-chlorophenyl)-2-phenyl-2H-indazole (3ra):
3-phenyl-2-(p-tolyl)-2H-indazole (3ab):
2-(4-(tert-butyl)phenyl)-3-phenyl-2H-indazole (3ac):
2-(3,5-dimethylphenyl)-3-phenyl-2H-indazole (3ad):
2-(4-chlorophenyl)-3-phenyl-2H-indazole (3ae):
2-(3-chlorophenyl)-3-phenyl-2H-indazole (3af):
2-(3-bromophenyl)-3-phenyl-2H-indazole (3ag):